

BATT TASK 1 CELL DEVELOPMENT

TASK STATUS REPORT

PI, INSTITUTION: K. Striebel, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Development - Cell Fabrication and Testing

SYSTEMS: Low-Cost Li-Ion, High-Power Li-Ion

BARRIER: Inconsistent evaluation of the merits of candidate novel materials.

OBJECTIVES: The primary objective is to establish a test vehicle for the evaluation of new materials for high-power and low-cost Li-ion cells.

APPROACH: The testing of novel materials in a standard cell with preset protocols will provide the necessary link between the invention of novel battery components and the diagnostic evaluation of failure modes, and will accelerate the development of a battery-powered EV. This task is a collaborative effort, which includes the development of an appropriate test vehicle (cell geometry), electrochemical cycling, and cell disassembly. Novel components will be developed in BATT Program Tasks 2, 3, and 4 (anodes, electrolytes, and cathodes) for baseline liquid and gel electrolyte chemistries. These components are incorporated into a standardized cell with appropriate ratios of components (*i.e.*, active materials/electrolyte volume) and tested with a consistent protocol to determine capacity, energy, power, and lifetime characteristics. Components are then delivered to the PI's involved with BATT Program diagnostics. Fabrication and testing of the third baseline cell, *i.e.*, Li metal/polymer/V₆O₁₃, will be carried out in the Electrolyte Task.

STATUS OCT. 1, 2000: This is a new project.

EXPECTED STATUS SEPT. 30, 2001: We expect to have semi-automated electrode preparation hardware in place. We expect to have pouch cell production hardware in place. We expect to have baseline evaluations of pouch cells (and Swagelok cells) carried out with baseline materials received from Quallion Corp. and a full testing protocol set up. We also expect to have a prototype web site set up with data from evaluation/testing of baseline cells from Doo Youn Corp. and Quallion Corp.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONE: Our milestone for the establishment of cell fabrication requires no further adjustment and should be met.

ACCOMPLISHMENTS TOWARD MILESTONE OVER LAST QUARTER:

1. Demonstrated that LBNL Li-ion pouch cells perform extremely well in comparison with high-quality Li-ion cells produced by Quallion Corporation.
2. Showed that the capacity retention of commercial Li-ion cells with graphite and LiCoO₂ electrodes is good at 25⁰C, but problems were apparent at 60⁰C.

3. Initial cycle-life tests of Li-on cells confirmed that: (a) power fade is a complicated issue, (b) correlating cell behavior with electrode/electrolyte interface design is an important goal, and (c) a new standard power/resistance test is necessary.

TASK STATUS REPORT

PI, INSTITUTION: T.J. Richardson, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Development - Materials Characterization Using X-Ray Diffraction and Chemical Analysis

SYSTEMS: Li/Polymer, Low-Cost Li-Ion

BARRIER: Short lithium battery lifetimes.

OBJECTIVES: Accelerate evaluation of electrode materials by structural characterization of active components as received (or synthesized), following cell disassembly, and *in situ* during cycling. Assist in electrode materials development.

APPROACH: Analyze cycled electrodes taken from baseline BATT Program cells, seeking deleterious phase transformations in the bulk of the active material and accumulated inactive decomposition products.

STATUS OCT. 1, 2000: This is a new task.

EXPECTED STATUS SEPT. 30, 2001: Establish active material compositions of cycled and uncycled electrodes from Cell Development and Cathode investigators (Striebel and Doeff). Correlate phase transformations and accumulation of decomposition products with cell cycling performance.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONE: Determine phase compositions in cycled electrode materials by the planned date of June 1, 2001.

ACCOMPLISHMENTS TOWARD MILESTONE OVER LAST QUARTER:

1. Examined cycled BATT Program electrodes for evidence of phase transitions using x-ray diffraction and infrared spectroscopic techniques.
2. Confirmed the good overcharge-overdischarge stability of LiFePO_4 cathodes.
3. Synthesized and characterized alternative cathode materials, including $\text{Li}_2\text{NiFPO}_4$, $\text{Li}_2\text{CoFPO}_4$, $\text{Na}_2\text{MnFPO}_4$, and FeOF .

BATT TASK 2 ANODES

TASK STATUS REPORT

PI, INSTITUTION: K. Kinoshita, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Anodes - Carbon Materials

SYSTEMS: Low-Cost Li-Ion

BARRIER: High Cost of Li-Ion Batteries

OBJECTIVES: The primary objective is to identify a low-cost carbon (<\$10/kg) for negative electrodes in Li-ion batteries for electric and hybrid vehicles.

APPROACH: We will continue our collaboration with industry (mainly HydroQuébec) to develop low-cost carbons for Li-ion batteries. Our role will be to utilize the analytical and spectroscopic facilities at LBNL to characterize the properties of the carbons. Techniques such as high-resolution electron microscopy, scanning electron microscopy, Raman spectroscopy, X-ray diffraction analysis and thermal analysis will be used to determine the physicochemical properties of carbon. Electrochemical studies to determine the reversible capacity and irreversible capacity loss of the carbons will be conducted in laboratory-scale cells.

STATUS OCT. 1, 2000: Our results suggest that there is a strong correlation between the irreversible capacity loss and the relative fraction of edge sites associated with the graphitized carbon sample. Within the range of graphite particle sizes considered in the study, there is no significant correlation between reversible capacity and the structural parameters associated with the crystallite size (*i.e.*, L_c , L_a). These results were obtained at reasonably low charge/discharge rates. We plan to examine these effects at higher rates to determine the influence of particle size on the initial reversible capacity. The correlation with cycle life was not investigated because we are not confident that the cells available (in-house) are adequate for cycle testing. This study was conducted in collaboration with HydroQuébec.

EXPECTED STATUS SEPT. 30, 2001: We expect to identify a chemical procedure to purify natural graphite that is lower cost than thermal purification processes. The samples will be evaluated in LiPF_6 -EC-EMC, LiTFSI + cross-linked PEO, and LiBF_4 + cross-linked gel electrolytes to determine their electrochemical performance compared to baseline systems.

RELEVANT USABC GOALS: Develop low-cost carbon to meet the cost target for battery of <\$150/kWh.

MILESTONE: Complete analysis of particle-size effect on high-rate charge/discharge of flake graphite in liquid electrolyte. (03/01)

ACCOMPLISHMENTS TOWARD MILESTONE OVER LAST QUARTER:

1. Completed analysis of particle-size effect on the high-rate charge/discharge of flake graphite in liquid electrolyte.
2. Demonstrated that flake natural graphite with 12 μm particle size may provide an optimum combination of high anode reversible capacity ($x > 0.8$ in Li_xC_6) and minimal irreversible capacity loss ($< 35 \text{ mAh/g}$).

TASK STATUS REPORT

PI, INSTITUTION: G.A. Nazri and D. Curtis, University of Michigan

TASK TITLE – PROJECT: Anodes - Optimization of Anodes for Li-Ion Batteries

SYSTEMS: Low-Cost Li-Ion

BARRIER: Safety, irreversible capacity loss, and self-discharge.

OBJECTIVES: The primary objective is to improve the overall safety, cycle life, and shelf life of the Li-ion battery, through development of a low-cost surface treatment process to stabilize the anode/electrolyte interface and reduce cell impedance.

APPROACH: Our approach is to stabilize the anode/electrolyte interface to prevent self-discharge, electrolyte decomposition, and improve safety aspects of the Li-ion battery. We are engineering an artificial SEI layer on anodic materials to provide a superior thermal and chemical stability, as well as a high Li-ion conductivity for application in high-power Li-ion batteries. The work is focused on the ATD Program Gen 2 chemistry, as well as the application of EC-EMC electrolytes for sub-ambient temperature performance.

STATUS OCT. 1, 2000: We developed a Li-phosphonate based polymer stable in the operational voltage range of carbonaceous anodes with the added benefit of fire-retardant properties. We also developed a unique *in situ* technique to explore the reactivity of anode/electrolyte interfaces.

EXPECTED STATUS SEPT. 30, 2001: We expect to fully incorporate the artificial SEI layer on a carbonaceous anode, and provide test results for improved rate capability, safety, and compatibility with a lower cost and more stable electrolyte. The process developed in this research will also remove undesirable impurities and reactive surface groups from carbonaceous anodes. We expect also to provide a working mechanism and a model for the artificial SEI layer to guide the scale-up of this invention. This research work expects to provide a practical graphite anode for Li-ion technology.

RELEVANT USABC GOALS: Improved safety of Li-ion batteries, long cycle and shelf life, compatibility for high-power batteries.

MILESTONES: Our milestones to synthesize and coat the anode with an artificial SEI, and provide performance test results are expected to be completed by the planned date, September 2001.

ACCOMPLISHMENTS TOWARD MILESTONES OVER LAST QUARTER:

1. Showed that EC and DMC phase separate below -10°C , thereby deteriorating Li-ion cell rate capability and cycle-life performance.
2. Demonstrated that PC can be added to blended carbonate solvents without producing unwanted side reactions with graphite, due to preferential solvation of Li^{+} ions by linear carbonates.

TASK STATUS REPORT

PI, INSTITUTION: M. Thackeray, Argonne National Laboratory

TASK TITLE: Anodes - Non-Carbonaceous Materials

SYSTEMS: Low-Cost Battery

BARRIER: Cost and safety limitations of Li-ion batteries.

OBJECTIVES: To replace carbon with an alternative inexpensive anode material that will be compatible, in particular, with low-cost manganese oxide cathodes. The project also addresses the need for improved safety of Li-ion cells.

APPROACH: Our approach is to search for, characterize, and develop inexpensive intermetallic electrodes that provide an electrochemical potential a few hundred mV above the potential of metallic Li, and that provide capacities >400 mAh/g and >1000 mAh/ml (the theoretical capacities for graphite are 372 mAh/g and 818 mAh/ml, respectively). The task entails the synthesis and electrochemical evaluation of the intermetallic electrodes and their structural characterization by X-ray diffraction and spectroscopy. The reactivity of the intermetallic electrodes with the electrolyte will be determined by calorimetric techniques.

STATUS OCT. 1, 2000: We have identified intermetallic compounds with nickel-arsenide and zinc-blende structure types for possible exploitation as anodes for Li batteries. Cu_6Sn_5 and InSb were identified as test cases for the preliminary investigations of these types of materials, respectively; they yield reversible capacities of 200 mAh/g and >1000 mAh/ml for 10-15 cycles. These novel materials have exciting prospects for further development and improvement in performance.

EXPECTED STATUS SEPT. 30, 2001: Improvements in electrochemical performance from either new or modified intermetallic electrode compositions based on tin and antimony compounds will have been achieved. We expect to have improved the cycling stability of these materials with reversible capacities of 250 mAh/g and >1000 mAh/ml for 40 cycles. We will have obtained preliminary data regarding the thermal stability of the intermetallic electrodes with respect to organic-based electrolytes. We will also have gathered a more detailed understanding of the behavior of NiAs and zinc-blende electrodes in electrochemical cells.

RELEVANT USABC GOALS: 10-year life, $<20\%$ fade over a 10-year period.

MILESTONES: The primary milestone will be to increase the reversible electrochemical capacity of tin- and antimony-based electrodes from 200 to 250 mAh/g for 20 cycles by the end of April 2001, by which time preliminary calorimetric data will also have been gathered. A target of reaching a capacity of 250 mAh/g for 40 cycles by end of September 2001 has been set, by which time a greater insight of the electrochemical mechanisms of tin- and antimony-based systems will also have been gathered to enable the identification of cost-effective intermetallic electrode structures.

ACCOMPLISHMENTS TOWARD MILESTONES OVER LAST QUARTER:

1. Achieved >200 mAh/g for >20 cycles with a novel non-carbonaceous Li_xInSb anode.
2. Achieved >290 mAh/g for >25 cycles with a novel non-carbonaceous $\text{Li}_x\text{Cu}_2\text{Sb}$ anode.

TASK STATUS REPORT

PI, INSTITUTION: M.S. Whittingham, SUNY at Binghamton

TASK TITLE - PROJECT: Anodes - Novel Materials

SYSTEMS: Low-Cost Li-Ion Battery and Gel Battery.

BARRIER: Cost, safety and volumetric capacity limitations of lithium-ion batteries

OBJECTIVES: To replace the presently used carbon anodes with safer materials that will be compatible with manganese oxide cathodes and the associated electrolyte.

APPROACH: Our anode approach is to explore, synthesize, characterize, and develop inexpensive materials that have a potential about 500 mV above that of pure Li (to minimize the risk of Li plating and thus enhance safety) and have higher volumetric energy densities than carbon. We will place emphasis on simple metal alloys. All materials will be evaluated electrochemically in a variety of cell configurations, and for thermal and kinetic stability.

STATUS OCT. 1, 2000: We have determined that vanadium and manganese oxides, in their highest oxidation states, are probably not prime candidates. Pure aluminum was found to have a high capacity and to react readily with Li, but its capacity faded rapidly on cycling. Some simple binary alloys of aluminum and of tin have been identified and are being evaluated.

EXPECTED STATUS SEPT. 30, 2001: We expect to improve the electrochemical performance of the materials identified, to have completed a survey of all Al-based binary systems and their reactivity with Li, and to have identified several additional non-Al binary alloys. We will complete a study of the lower-valent MnV_2O_5 oxide.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our major milestone is to identify, by September 2001, a new simple material (a binary alloy) that has the potential of higher volumetric capacity than carbon at about 0.5 V relative to pure Li. In addition, we will identify all known Al binary alloys and their ability to react with Li by August 2001, and our assessment of MnV_2O_5 as an anode material will be completed by April 2001.

ACCOMPLISHMENTS TOWARD MILESTONES OVER LAST QUARTER:

1. Halted work on manganese -vanadium oxides and aluminum alloys as candidate non-carbonaceous anodes due to inadequate performance and stability.
2. Continuing work on promising Sn_2Mn alloy anodes.

BATT TASK 3 ELECTROLYTES

TASK STATUS REPORT

PI, INSTITUTION: J. Kerr, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Electrolytes - R&D for Advanced Lithium Batteries

SYSTEMS: Li/Polymer and Low-Cost Li-Ion

BARRIERS: Short Li battery lifetimes, poor ambient-temperature performance for polymer electrolytes, and low energy and power densities as a result of polymer instability to 4-V cathodes.

OBJECTIVES:

- Determine the feasibility of the Li metal electrode with organic electrolytes and provide operating conditions that prevent dendrite growth.
- Determine the limitations on Li-ion transport in polymer electrolytes and composite electrodes and develop new materials capable of ambient-temperature operation with Li metal.
- Determine the limits of stability of organic electrolytes at high-voltage cathode materials (4 V) and develop materials and methods to increase stability.

APPROACH: Through a balance of synthesis, analysis, and modeling, a physical organic chemistry approach is taken to electrolyte design, thereby ensuring that not only are the sources of poor performance and failure pinpointed but the problem can be corrected through the materials design and synthesis capabilities thereby developed.

STATUS OCT. 1, 2000: Polymer synthesis capability has been established that facilitates the production of linear and branched polymer networks for use in Li/polymer batteries and polymer gel Li-ion systems. New polymers with significantly higher conductivities are now available as are polymer systems with higher voltage stabilities than PEO.

EXPECTED STATUS SEPT. 30, 2001: We expect to complete a study of the effects of mechanical, chemical, and transport properties of polymer electrolytes on dendrite growth at Li metal electrodes that will provide data to allow the system to be accurately modeled. We expect to prepare and test polymer electrolytes with room-temperature performance and to define the upper limits of ion transport for polymer electrolytes. We expect to determine the practical cathode stabilities of polymer electrolytes with adequate transport properties.

RELEVANT USABC GOALS: 10 year life, <20% capacity fade over a 10-year period, 1000 cycles, operating environment -40 to 65°C, specific energy >170 Wh/kg, specific power >300 W/kg, <150\$/kWh @ 20K/year.

MILESTONES:

1. Determine electrolyte properties that inhibit dendrite growth (September 30, 2001).
2. Determine the limits of Li ion mobility in polymer electrolytes (September 30, 2001).
3. Prepare bulk materials (100g) for testing in the BATT Li polymer (April 15, 2001) and low-cost Li-ion test systems (June 30, 2001).

ACCOMPLISHMENTS TOWARD MILESTONES OVER LAST QUARTER:

1. Demonstrated that the cross-link density of polymer electrolytes affects Li dendrite growth.
2. Evaluated the conductivities of linear and comb-branch polymer electrolytes with different solvating groups.

TASK STATUS REPORT

PI, INSTITUTION: S.A. Khan, P.S. Fedkiw, North Carolina State University; G.L. Baker, Michigan State University

TASK TITLE - PROJECT: Electrolytes - Composite Polymer Electrolytes for Lithium and Lithium-Ion Batteries

SYSTEMS: Li/Polymer

BARRIER: Short lithium battery lifetimes and high costs.

OBJECTIVES: The ultimate objectives are to develop composite polymer electrolytes that are low-cost, have high conductivities, impart electrode-electrolyte interfacial stability, and yield long cycle life.

APPROACH: Our approach is to use surface-functionalized fumed silica fillers in BATT-baseline systems to determine the effects of filler type and concentration on interfacial stability and cell cycling. We intend to correlate these electrochemical characteristics with mechanical properties and materials chemistry (*e.g.*, silica-type or PEO-type, synthesized by Baker or Kerr, respectively). Data to be collected include modulus, ionic conductivity, Li cycling efficiency, Li-electrolyte interfacial resistance, and full-cell cycling capacity using 3-V cathodes.

STATUS OCT. 1, 2000: We established that fumed silica-based composite electrolytes with low-molecular weight PEOs exhibit conductivities exceeding 10^{-3} S/cm at 25°C; have electrochemical properties (Li transference number, conductivity) decoupled from mechanical properties, thus providing a range of mechanical modulus (as high as 10^6 Pa); and, the presence of fumed silica enhances Li-electrolyte interfacial stability, although the extent and mechanism remain to be determined.

EXPECTED STATUS SEPT. 30, 2001: We expect to determine how fumed silica (hydrophobic R805 and hydrophilic A200) affect full-cell cycling using vanadium-based, 3-V cathodes and baseline PEO-type materials in coin cells. We also expect to identify to what extent fumed silica enhances interfacial stability in low-molecular-weight PEOs and begin extending the analysis to base-line PEO materials. We expect to characterize how interfacial stability is related to the mechanical properties, working in close collaboration with J. Kerr.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our major milestone to determine the effects of fumed silica (hydrophobic R805 and hydrophilic A200) on full-cell cycling and interfacial stability is expected to be completed by September 2001.

ACCOMPLISHMENTS TOWARD MILESTONES OVER LAST QUARTER:

1. Demonstrated that using fumed silica to prepare composite polymer electrolytes not only increases Li electrode cycle performance and Li/V₆O₁₃ cell capacity, but also allows one to tailor the electrolyte mechanical properties.
2. Showed that fumed silica additions have negligible effects on polymer electrolyte ionic conductivity, lithium diffusion coefficient, and cation transference number.

TASK STATUS REPORT

PI, INSTITUTION: D.F. Shriver, S. Vaynman, Northwestern University

TASK TITLE - PROJECT: Electrolytes - Highly Conductive Polyelectrolyte-Containing Rigid Polymers

SYSTEMS: Li/Polymer

BARRIER: Low ionic conductivity of the polymer electrolyte, electrochemical instability of the polymer electrolyte toward Li electrodes.

OBJECTIVES: The primary objective is to synthesize and test a new class of highly ionic-conductive, rigid polymer electrolytes for rechargeable Li batteries.

APPROACH: Our approach is to modify the highly ion-conductive rigid polymer electrolytes previously synthesized at Northwestern University by replacing electrochemically unstable carboxy groups with more inert oxygen-rich functional groups such as sulfones, thus increasing the stability of the electrolyte toward the Li electrode. If this or related instabilities with sulfone-containing polymer electrolytes are encountered, we will prepare new polymer electrolytes. One such possibility is a bilayer electrolyte with an oxidation-resistant fluorocarbon backbone on one side and a reduction-resistant hydrocarbon or hydrocarbon ether backbone on the surface in contact with the Li electrode. At least two polymer-salt complexes and polyelectrolytes will be synthesized, and their properties will be measured. These electrolytes will be tested in Li cells. Before polymers are synthesized we will test the stability of the small-molecule analogs of the polymers in contact with Li metal.

STATUS OCT. 1, 2000: We synthesized highly conductive rigid polymer electrolytes that contain functional groups such as carboxy and sulfone and tested them in cells. Polymer-salt complexes that contain carboxy groups have high ionic conductivity ($\sim 10^{-4}$ S/cm at room temperature), but are unstable toward Li. The ionic conductivity of a recently synthesized polymer-salt complex that contains sulfone functional groups is lower ($\sim 5 \times 10^{-6}$ S/cm at room temperature), but the stability toward Li is much higher than that of polymer-salt complexes that contain carboxy groups.

EXPECTED STATUS SEPT. 30, 2001: We expect to synthesize and test in cells a number of sulfone-containing rigid polymer electrolytes and polyelectrolytes that display favorable ionic conductivity and good electrochemical stability toward battery components. Also, we expect to scale up the synthesis of the most promising electrolyte(s) and send them to LBNL for large-scale testing.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our major milestones are:

1. To synthesize and test promising polymer systems by 6/2001 with the goal of conductivity higher than 10^{-4} S/cm at room temperature. The resistivity of the Li/polymer electrolyte cell should not increase more than twice during the first week of testing.
2. To scale-up the synthesis of the most promising polymer electrolyte and to send it by 10/2001 to LBNL for cell fabrication and testing.

ACCOMPLISHMENTS TOWARD MILESTONES OVER LAST QUARTER:

1. Prepared polysulfone-based electrolytes with conductivity $\sim 10^{-4}$ S/cm.
2. Found that polysulfone-based electrolytes exhibit better stability than poly(dioxolane-oxalate) electrolytes, but more work is needed to demonstrate their feasibility.

TASK STATUS REPORT

PI, INSTITUTION: K. Kinoshita, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Electrolytes - Electrolyte Additives

SYSTEMS: Low-Cost Li-Ion

BARRIER: Safety of Li-Ion Batteries

OBJECTIVES: The primary objective is to identify chemical additives that improve the safety of nonaqueous electrolytes for Li-ion batteries by stabilizing the SEI layer on carbon.

APPROACH: A study will be undertaken to identify suitable additives that function as a radical trap for the radical anions produced by solvent reduction. We propose to use this concept to identify species that are incorporated in the SEI layer to improve its stability. This type of reaction product will be evaluated as additives in gel and liquid electrolytes. Based on our studies of reaction products obtained by thermal decomposition of the electrolyte, compounds that decompose to form polyether and polycarbonate oligomers will be studied as additives. Electrochemical evaluation of additives to determine the reversible and irreversible capacity loss will be conducted in coin cells using the baseline liquid or gel electrolytes. TEM and AFM will be used to study the effect of additives on the thickness and structure of the SEI layer and the irreversible capacity loss of carbon electrodes. Thermal analysis studies will be used to determine the thermal stability of carbon electrodes containing a SEI layer.

STATUS OCT. 1, 2000: Experiments were initiated to determine the thermal stability of a baseline electrolyte [1 M LiPF₆ in a mixture of 1:1 EC/DMC]. The electrolyte was heated to 85°C, and samples were removed periodically for analysis by gas chromatography (GC). The GC trace from the electrolyte mixture shows two clearly separate solvent peaks for DMC (5-min retention time) and EC (about 14.1-min retention time) as well as a large new peak at 13.8-min retention time and several others of lower intensity. The peak intensity for EC decreases as a function of storage time, indicative of the gradual decomposition of EC at 85°C. On the other hand, the GC signal for DMC remains essentially constant in intensity, indicating that DMC is stable during storage at 85°C. The major new compound was identified as diethyl 2,5 dioxahexane carboxylate (DEDOHC), which increases with time of storage at 85°C.

EXPECTED STATUS SEPT. 30, 2001: We expect to identify a chemical additive that enhances the thermal stability of the SEI layer on carbon. The additives will be evaluated in a liquid electrolyte to determine their electrochemical performance compared to baseline systems.

RELEVANT USABC GOALS: Identify additives that improve the safety of Li-ion batteries.

MILESTONES:

1. Identify desired structural features of additives that enhance SEI properties (12/00).
2. Evaluate the effect of polycarbonates as additives for improving the thermal stability of the SEI layer on carbon electrodes (9/01).

ACCOMPLISHMENTS TOWARD MILESTONES OVER LAST QUARTER:

1. Completed analyses of poly(ether-carbonate) as an electrolyte additive to facilitate SEI formation, but results indicated little benefit.

2. Completed analyses of pyrrole as an electrolyte additive to facilitate SEI formation, but results indicated little benefit.

TASK STATUS REPORT

PI, INSTITUTION: J. Prakash, Illinois Institute of Technology

TASK TITLE - PROJECT: Electrolytes - Nonflammable Electrolytes and Thermal Characterization

SYSTEMS: Li/Polymer and Low-Cost Li-Ion

BARRIER: Thermal safety

OBJECTIVES: The goal of this proposal is to assist DOE/BATT in developing advanced high-performance Li-ion cells for electric and hybrid vehicles. The objectives of this project are: (1) to develop nonflammable electrolytes with high flash point ($>100^{\circ}\text{C}$), ionic conductivity (10^{-3} S/cm), and wider voltage window (0-5 V vs. Li); and (2) to evaluate anode and cathode (being developed in the BATT Program) materials in coin cells using thermal diagnostic methods.

APPROACH: Our research approach will include (1) the development of thermally stable and nonflammable electrolytes to provide safety and (2) thermal diagnostic studies of the baseline Li-polymer and low-cost Li-ion cells using differential scanning calorimetry (DSC), isothermal microcalorimetry (IMC), and accelerated rate calorimetry (ARC) in order to understand the degradation, failure, and safety mechanisms.

STATUS OCT. 1, 2000: We completed the synthesis of the flame retardant (FR) hexa-methoxy-tri-aza-phosphazene $\text{N}_3\text{P}_3[\text{OCH}_3]_6$ and supplied 10 grams of this material to the ATD Program (ANL and PolyStor) for further testing in PNGV Li-ion cells. We also completed the thermal and electrochemical characterization of this FR additive in Li-ion cells using cyclic voltammetry, AC-impedance, cell cycling, DSC, and ARC.

EXPECTED STATUS SEPT. 30, 2001: We expect to synthesize two flame-retardant additives, hexa-ethoxy-tri-aza-phosphazene (HETAP) and urea-diphosphonate (URDP), and characterize their electrochemical and thermal behavior in low-cost Li-ion cells. We also expect to complete the synthesis and characterization of two thermally stable and corrosion-resistant modified imide salts $\text{LiN}(\text{SO}_2\text{X})_2$ ($\text{X} = -\text{CF}(\text{CF}_3)_2$ and $-\text{C}(\text{CF}_3)_3$). In addition, we expect to characterize the thermal behavior of Li-ion cells containing graphite and Sn-based anodes, $\text{LiAl}_{0.05}\text{Ni}_{0.8}\text{Co}_{0.15}\text{O}_2$ and $\text{Li}_{1.02}\text{Al}_{0.25}\text{Mn}_{1.75}\text{O}_{3.92}\text{S}_{0.03}$ cathode in LiPF_6 -EC-EMC and LiBF_4 + cross-linked gel electrolyte.

RELEVANT USABC GOALS: Thermal and fire safety of the EV batteries under normal and abusive conditions.

MILESTONES:

1. The scale-up synthesis of the FR additive HMTAP and the thermal characterization of the FR additive HETAP are expected to be completed by the planned date of April 2001.
2. The thermal characterization of graphite anode (for comparison purposes) using IMC and DSC is also expected to be completed by April 2001.

ACCOMPLISHMENTS TOWARD MILESTONES OVER LAST QUARTER:

1. Discovered that the novel hexa-methoxy-cyclo-triphosphazene flame-retardant additive delayed Li-ion cell self heating by $\sim 20^{\circ}\text{C}$, but cell self heating was increased at higher temperatures.
2. Began work on the new flame-retardant additive urea-diphosphonate.

BATT TASK 4 CATHODES

TASK STATUS REPORT

PI, INSTITUTION: M. Thackeray, Argonne National Laboratory

TASK TITLE: Cathodes - Novel Materials

SYSTEMS: Low-Cost (Li-Ion) Battery and Li-Polymer Battery

BARRIER: Cost limitations of Li-ion and Li-polymer batteries

OBJECTIVES: To develop low-cost manganese-oxide cathodes to replace vanadium oxide electrodes in Li-polymer cells and cobalt/nickel electrodes in Li-ion cells.

APPROACH: Our approach is to search for, characterize, and develop low-cost manganese oxide electrodes that can be used in Li-ion and Li-polymer cells; the electrodes will be synthesized in the discharged and charged states, respectively. For Li-ion cells, focus will be placed on layered lithium-manganese oxide structures that do not convert to spinel upon electrochemical cycling, particularly those derived from Li_2MnO_3 ; for Li-polymer cells, the material of choice is stabilized $\alpha\text{-MnO}_2$. (Note: At this stage of the project, we have downgraded the research priority to search for an alternative vanadium oxide electrode, such as V_6O_{13} , to replace the current material of choice, LiV_3O_8 , because in the Li-V-O system, LiV_3O_8 is still believed to be the best vanadium oxide electrode available for Li-polymer cells.)

STATUS OCT. 1, 2000: We have exploited the concept of using a Li_2MnO_3 component to stabilize layered LiMO_2 structures with the ultimate objective of stabilizing layered LiMnO_2 . In particular, we expanded our synthesis efforts to include solid solutions of $[\text{x}(\text{Li}_2\text{MnO}_3)\bullet\text{y}(\text{LiMO}_2)]$ compositions, where M = Mn, Ni or Co, or a combination thereof. Optimized compositions have yielded specific capacities of ~150 mAh/g between 4.5 and 3.0 V in Li half-cells at 50°C, but for less than 100 cycles.

EXPECTED STATUS SEPT. 30, 2001: Improvements in the electrochemical performance of $[\text{x}(\text{Li}_2\text{MnO}_3)\bullet\text{y}(\text{LiMO}_2)]$ electrodes will have been achieved. A performance target of 150 mAh/g for 100 cycles at 50°C in Li/ $[\text{x}(\text{Li}_2\text{MnO}_3)\bullet\text{y}(\text{LiMO}_2)]$ cells has been set. A more detailed understanding of the behavior of $[\text{x}(\text{Li}_2\text{MnO}_3)\bullet\text{y}(\text{LiMO}_2)]$ electrodes will have been gathered. Work on stabilized $\alpha\text{-MnO}_2$ electrodes for Li-polymer cells will have been initiated in collaboration with LBNL (J. Kerr) with an initial target reversible capacity set at 200 mAh/g for 50 cycles.

RELEVANT USABC GOALS: 10-year life, <20% fade over a 10-year period.

MILESTONES: The initial milestone (#1) to be reached by the end of April 2001 will be to achieve a reversible electrochemical capacity of 150 mAh/g from layered $[\text{x}(\text{Li}_2\text{MnO}_3)\bullet\text{y}(\text{LiMO}_2)]$ electrodes for 50 cycles at 50°C against a metallic Li counter electrode. This will be increased to 100 cycles by the end of September 2001 (#2). By then a more detailed understanding of the electrochemical and structural relationships of layered $[\text{x}(\text{Li}_2\text{MnO}_3)\bullet\text{y}(\text{LiMO}_2)]$ electrodes will also have been gathered.

ACCOMPLISHMENTS TOWARD MILESTONES OVER LAST QUARTER:

1. Achieved >150 mAh/g for >10 cycles with a 0.2 Li_2MnO_3 – 0.8 $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode.

2. Achieved >200 mAh/g with a novel -MnO_2 cathode.

TASK STATUS REPORT

PI, INSTITUTION: M.S. Whittingham, SUNY at Binghamton

TASK TITLE - PROJECT: Cathodes – Novel Materials

SYSTEMS: Li/Polymer/Gel and Low-Cost Li-Ion

BARRIER: Lower-cost, higher-capacity and safer cathodes

OBJECTIVES: The primary objective is to find lower-cost and higher-capacity cathodes, exceeding 200 Ah/kg, that are based on benign materials.

APPROACH: Our cathode approach is to place emphasis on manganese dioxides, both pure and modified with other transition metals, using predominantly low-temperature synthesis approaches. These materials will be synthesized, and characterized both structurally and for thermal and chemical stability. All will be evaluated electrochemically in a variety of cell configurations.

STATUS OCT. 1, 2000: We determined that layered manganese dioxides can be structurally stabilized, that their stability is a function of current density and/or cut-off voltages, that their electronic conductivity can be significantly enhanced, that their cell cycling can be substantially improved by addition of other transition metals, and that hydrothermally synthesized manganese oxides cycle as well as high-temperature materials. We also showed that vanadium oxides can be stabilized by the addition of manganese ions

EXPECTED STATUS SEPT. 30, 2001: For low-cost Li-Ion cells, we expect to identify the changes in LiMnO_2 structure as a function of current density in cell cycling, to determine the structure and composition of the vanadium-stabilized LiMnO_2 and to increase its electrochemical capacity, to understand better the behavior of the $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Cr}_{0.4}\text{O}_2$ cathode and to determine if there is an iron analog. For Li/polymer cells we expect to complete the evaluation of the manganese-stabilized -vanadium oxides and to compare them to the iron phosphates. Emphasis in all cases will be placed on understanding the reasons for capacity fade.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our major milestones this year are:

1. To characterize the pillared manganese oxide, and improve its capacity to 150 mAh/g with an ultimate goal of 200 Ah/kg.
2. To complete the characterization of manganese-stabilized vanadium oxides and to compare the best samples with iron phosphates for polymer or gel batteries by July 2001.

ACCOMPLISHMENTS TOWARD MILESTONES OVER LAST QUARTER:

1. Demonstrated that vanadium-oxygen “pillars” appear to stabilize the MnO_2 cathode structure relative to the spinel structure.
2. Used a low-cost hydrothermal method to synthesize LiFePO_4 cathodes.

TASK STATUS REPORT

PI, INSTITUTION: M. Doeff, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cathodes -Synthesis and Characterization of Cathode Materials for Rechargeable Lithium and Lithium Ion Batteries

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIERS: Cost, cycle life, safety, and energy density

OBJECTIVES: To develop low-cost cathodes based on benign materials (*e.g.*, manganese oxides, lithium iron phosphates) having electrochemical characteristics (*e.g.*, cycle life, energy and power densities) consistent with the goals of the USABC and/or PNGV.

APPROACH: Cathode materials are synthesized using both conventional solid-state techniques and solution methods (*e.g.*, sol-gel, glycine-nitrate combustion). The micro-structures and atomic structures of the materials are determined by relevant methods, and electrochemical analysis is carried out in a variety of cell configurations. Emphasis is placed on structurally stable materials such as tunnel-containing manganese oxides, as well as those of commercial interest, such as spinels and lithium iron phosphate.

STATUS OCT. 1, 2000: A tunnel-containing manganese oxide has been cycled more than 700 times in a Li/liquid electrolyte cell configuration, with little capacity loss and no structural change. Cells can be discharged repeatedly at up to 5 C rate with no damage. The effect of Ti-substitution upon the electrochemical characteristics has been determined, and a correlation between unit cell size and capacity has been observed.

EXPECTED STATUS SEPT. 30, 2001: The program will be expanded to include lithium iron phosphates and substituted spinels as required by the BATT program. We expect to have prepared samples of LiFePO_4 available for the program and to have made a preliminary determination of the electrochemical characteristics. We also will have determined if anion substitution of tunnel-containing manganese oxides is a viable approach to improving capacity.

RELEVANT USABC GOALS: 10-year life, < 20% capacity fade over a 10-year period.

MILESTONES: Our major milestone this year is to provide small samples (30 g) of conventional LiFePO_4 to the BATT program by early 2001. We are slightly delayed because of a furnace problem, which should be fixed shortly. As a substitute until we can provide the LiFePO_4 , we have delivered a sample of Li_xMnO_2 for use in baseline cells.

ACCOMPLISHMENTS TOWARD MILESTONES OVER LAST QUARTER:

1. Demonstrated good performance of a Li/polymer/ LiFePO_4 cell, but careful attention must be paid to electrode fabrication details.
2. Continued work on anion substitution to modify tunnel-structure Li_xMnO_2 cathodes.

BATT TASK 5 DIAGNOSTICS

TASK STATUS REPORT

PI, INSTITUTION: F. McLarnon, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics - Electrode Surface Layers

SYSTEMS: Li/Polymer and Low-Cost Li-Ion

BARRIER: Short lithium battery lifetimes

OBJECTIVES: The primary objective is to establish direct correlations between electrode surface changes, interfacial phenomena, and cell capacity decline.

APPROACH: Our approach is to use ellipsometry, Raman spectroscopy, and advanced microscopic techniques to characterize electrodes taken from baseline BATT Program cells, as well as thin-film electrodes in model cells. Data to be collected include changes in electrode surface morphology, electrode surface chemistry, and SEI thickness and composition, which accompany cell cycling.

STATUS OCT. 1, 2000: We defined the relationships between electrode history, electrolyte composition, electrode surface properties, and temperature for a model thin-film spinel LiMn_2O_4 cathode.

EXPECTED STATUS SEPT. 30, 2001: We expect to identify changes in $\text{LiAl}_{0.05}\text{Ni}_{0.80}\text{Co}_{0.15}\text{O}_2$ and $\text{Li}_{1.02}\text{Al}_{0.25}\text{Mn}_{1.75}\text{O}_{3.92}\text{S}_{0.03}$ cathode surface morphology and chemistry which accompany cycling in LiPF_6 -EC-EMC, LiTFSI +cross-linked PEO, and LiBF_4 + cross-linked gel electrolytes, and identify or confirm specific degradation modes. We expect to characterize SEI formation and growth on Li and carbonaceous anodes in LiPF_6 -EC-EMC, LiTFSI +cross-linked PEO, and LiBF_4 + cross-linked gel electrolytes, and determine the role of SEI growth in cell capacity and power loss.

RELEVANT USABC GOALS: 0 year life, < 20% capacity fade over a 10-year period.

MILESTONE: Our major milestone to determine the effect of sulfur additives on the surface chemistry of LiMn_2O_4 electrodes is expected to be completed by the planned date of April 2001, or shortly thereafter.

ACCOMPLISHMENTS TOWARD MILESTONE OVER LAST QUARTER:

1. Demonstrated unexpected nonuniform state of charge on cathodes taken from cycled BATT Program cells.
2. Used confocal Raman microscopy to provide strong evidence of crystal disorder, surface film formation, and new oxide phase formation in cathodes taken from cycled BATT Program cells.

TASK STATUS REPORT

PI, INSTITUTION: J. McBreen Brookhaven National Laboratory

TASK TITLE - PROJECT: Diagnostics - Structure and Characterization of Materials

SYSTEMS: Low-Cost Li-Ion

BARRIER: Short lithium battery lifetimes

OBJECTIVES: The primary objective is to establish direct correlations between electrode materials changes, interfacial phenomena, and cell capacity decline.

APPROACH: Our approach is to use a combination of *in situ* and *ex situ* synchrotron techniques to characterize electrode materials and electrodes taken from baseline BATT Program cells. Techniques that are sensitive to both bulk and surface processes will be used. This will include both K and L-edge X-ray absorption spectroscopy and transmission electron microscopy (TEM).

STATUS OCT. 1, 2000: We have completed an extensive study of the effect of Li and O stoichiometry on the phase behavior of spinel LiMn_2O_4 cathodes during cycling at ambient and at low temperatures. The effects of electrode history on the phase behavior of LiMn_2O_4 cathodes were also investigated.

EXPECTED STATUS SEPT. 30, 2001: We expect to identify the changes in $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_2$ and $\text{Li}_{1.02}\text{Al}_{0.25}\text{Mn}_{1.75}\text{O}_{3.92}\text{S}_{0.03}$ when cycled in $\text{LiPF}_6\text{-EC-DMC}$ electrolyte. We also expect to develop a combination of electron yield and fluorescent XAS at transition metal K- and L-edges as a tool for identification of inorganic surface degradation products in cathodes.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES:

1. Completion of XAS studies of LiCrMnO_2 by April 2001.
2. Completion of XRD and XAS studies of $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ by June 2001.
3. Develop a combination of electron yield and fluorescent XAS at transition metal K- and L-edges as a tool for identification of inorganic surface degradation products in cathodes by September 30, 2001.
4. Determine electrolyte effect on stability of LiMn_2O_4 at elevated temperatures by December 30, 2001.

ACCOMPLISHMENTS TOWARD MILESTONES OVER LAST QUARTER:

1. Used X-ray absorption techniques to demonstrate that toxic Cr^{6+} forms in the new $\text{Li}[\text{Li}_{0.2}\text{Cr}_{0.4}\text{Mn}_{0.4}]\text{O}_2$ electrode, and that the Mn is inactive during its oxidation and reduction.
2. Developed and applied electron-yield x-ray absorption spectroscopy techniques to study surface processes at electrodes.

TASK STATUS REPORT

PI, INSTITUTION: P.N. Ross, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics – Interfacial and Reactivity Studies

SYSTEMS: Low-Cost Li-Ion

BARRIER: Short lithium battery lifetimes

OBJECTIVES: The primary objective is to establish direct correlations between electrode surface changes, interfacial phenomena, and cell failure.

APPROACH: Our approach is to use Fourier transform infrared (FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) to study model electrode/electrolyte combinations, *e.g.*, using glassy carbon electrodes and BATT Program electrolytes, to provide the basis to interpret more-complex spectra recorded for ATD Program cell materials.

STATUS OCT. 1, 2000: We identified one of the mechanisms of SEI layer formation on carbon anode in EC-based electrolytes.

EXPECTED STATUS SEPT. 30, 2001: Establish thermal stability of the SEI layer on graphite anodes in GEN 2 electrolyte. Identify some routes to improved stability *via* electrolyte additives and/or graphite pre-treatment.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our major milestone to install and calibrate a new IR microscope is postponed to April 2001 due to the delay of equipment funds. Another new milestone is set to demonstrate that one of our diagnostic techniques can identify a failure mechanism in a Li-ion battery.

ACCOMPLISHMENTS TOWARD MILESTONES OVER LAST QUARTER:

1. Used molecular orbital theory and density function calculations to analyze details of solvent oxidation and reduction.
2. Showed that the cell stability window for all common etheric and carbonate solvents is ~4 V.

TASK STATUS REPORT

PI, INSTITUTION: E.J. Cairns, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics - Synthesis and Characterization of Electrodes

SYSTEMS: Li-Ion and Li-polymer Batteries

BARRIER: Rapid capacity fade

OBJECTIVES: The primary objectives are (1) to directly observe Li in BATT Program cathode materials, characterize the Li atomic and electronic local environment, and determine changes in this environment with cycling; and (2) to synthesize intermetallics that have higher capacities than carbon electrodes and that demonstrate stable capacities during cycling.

APPROACH: Our approach is to use ^7Li MAS-NMR to characterize electrodes before and after cycling. Data to be collected are isotropic chemical shift, linewidth, and relaxation times for each species of Li. We prepare intermetallics in the Mg-Sn system by mechanical alloying. Characterizations are performed with X-ray diffraction and microscopy techniques.

STATUS, OCT. 1, 2000: Milling conditions to synthesize cubic and rhombohedral forms of Mg_2Sn were determined. Amorphous Mg-Sn alloys could not be produced by mechanical alloying in a typical high-power ball-mill. Attempts to synthesize a metastable, cubic $\text{Mg}_{5.67}\text{Sn}$ alloy were started. Cycling tests showed that cubic- Mg_2Sn capacities can exceed capacities for carbon electrodes, but the capacities fade below 100 mAh/g after a few cycles. Comparisons between fine-grained Mg_2Sn and coarse-grained Mg_2Sn show that the microstructure of these intermetallics influences electrochemical performance. X-ray diffraction of cycled electrodes indicates that a major mechanism for the capacity decay is conversion of the intermetallic into Mg and Sn.

EXPECTED STATUS SEPT. 31, 2001: We expect to have concluded our evaluation of the Mg-Sn system. We plan to perform nuclear magnetic resonance experiments to aid in the characterization of the microstructure of the intermetallics and to determine sites that are occupied by Li. We expect to have identified the role of the microstructure in Mg_2Sn , studied through experiments on as-milled samples and on annealed samples, on the electrode capacity and cycle life. Similar work will be performed on the metastable, rhombohedral- Mg_2Sn phase to determine if this more conductive phase retains its structure during cycling.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: Our major milestones are to compare NMR-observable properties of stoichiometric and substituted tunnel-structure electrodes before and after cycling, and to complete work on the cubic- Mg_2Sn phase by April 2001.

ACCOMPLISHMENTS TOWARD MILESTONES OVER LAST QUARTER:

1. NMR measurements of Ti-substituted tunnel-structure LiMnO_2 cathodes demonstrated that Ti substitution affects the local Li environment.
2. Initial NMR measurements of LiFePO_4 cathode material produced no evidence for Li-O-Fe covalence.

3. Mg_2Si anode materials prepared by ball-milling exhibited an initial capacity of $>800 \text{ mAh/g}$, but the capacity decayed rapidly during cycling.

TASK STATUS REPORT

PI, INSTITUTION: J. Evans, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics - EQCM Studies of the SEI on Carbon Anodes

SYSTEMS: High-power Li-ion battery

BARRIER: Irreversible capacity loss due to SEI formation and growth

OBJECTIVES: The primary objective is to understand SEI formation and growth on carbon anodes.

APPROACH: Our approach is to use an electrochemical quartz crystal microbalance (EQCM) to characterize the SEI formed on disordered carbon thin-film electrodes in model cells. Data to be collected are changes in mass of the SEI on the electrode and, thereby, the SEI growth with cell cycling is studied. A joint study to combine spectroscopic ellipsometry and EQCM gives us the SEI density.

STATUS OCT. 1, 2000: We estimated the SEI density on disordered carbon thin-film electrodes and observed mass changes corresponding to Li intercalation/deintercalation in 1M LiClO₄/ EC+DMC electrolyte.

EXPECTED STATUS SEPT. 30, 2001: We expect to correlate SEI formation and growth with the electrolyte LiPF₆ or LiTFSI / EC+DMC electrolyte and impurities (*e.g.*, H₂O).

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONE: Our major milestone to study the dynamic nature of the SEI as a function of electrolyte composition during cycling is expected to be completed by the planned date of July 2001.

ACCOMPLISHMENTS TOWARD MILESTONE OVER LAST QUARTER:

1. The quartz crystal microbalance technique was used to characterize SEI formation on model thin-film carbon anodes, however the sensitivity of this technique was too low to allow significant conclusions to be drawn.
2. Studies on anode SEI formation will be concluded in FY 2001.

BATT TASK 6 MODELING

TASK STATUS REPORT

PI, INSTITUTION: J. Newman, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Modeling - Improved Electrochemical Models

SYSTEMS: Li/Polymer and Low-Cost Li-Ion

BARRIERS: Poor polymer transport properties, thermal management, dendrite formation

OBJECTIVES: Develop experimental and computational methods for measuring and predicting transport, kinetic, and thermodynamic properties. Model electrochemical systems to optimize performance, identify limiting factors, and mitigate failure mechanisms.

APPROACH: Use galvanostatic polarization technique to measure a complete set of transport properties, which aids selection of improved polymer electrolytes. Develop molecular dynamics program to predict diffusion coefficients in multicomponent solutions. Use potentiometric technique to measure entropy and develop thermal model that accounts for concentration effects in insertion electrodes, in order to improve thermal management. Develop model of factors affecting dendrite formation on Li metal. Use Raman spectroscopy to measure *in situ* concentration profile and dendrite growth.

STATUS OCT. 1, 2000: Measured transport properties in PEMO-LiTFSI polymer electrolyte and improved the measurement technique. Completed computer program and simulations for electrolyte diffusion coefficient of NaCl and KCl in water. Used calorimetry to validate energy balance. Measured entropy in manganese oxides. Developed a preliminary model for dendrite growth which includes effects of surface tension. Developing Raman spectroscopy methods to examine dendrite growth *in situ*.

EXPECTED STATUS SEPT. 30, 2001: We expect to complete measurements of the transport properties of PEMO-LiTFSI and to complete refinement of both the galvanostatic polarization method and the transition-time verification method. Modification of the molecular dynamics program to predict diffusion coefficients in multicomponent electrolytes currently of interest to the BATT program, such as LiBF₄ in EC:PC, will be ongoing. Measurements of the entropy of reaction in BATT baseline materials will be completed. Modeling of the SEI layer will be ongoing. Refinement of a model of dendrite growth to include relevant physical effects will be ongoing, as will experimental work to observe dendrite growth and concentration profiles *in situ* using confocal Raman spectroscopy.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, <20% capacity fade.

MILESTONES:

1. Preliminary model of transport through the SEI layer by August 1, 2001.
2. Design a cell container for *in situ* confocal Raman microscopy by July 1, 2001.

ACCOMPLISHMENTS TOWARD MILESTONES OVER LAST QUARTER:

1. Completed measurement of transport and thermodynamic properties for LiTFSI-PEMO electrolyte from 0.03 to 2.5 M at 85°C.
2. Completed transition-time measurements on LiTFSI-PEMO electrolyte and compared them to measured transport properties using simulations.

3. Verified the consistency between experiment and molecular dynamics modeling methods for simulating mass transport in aqueous electrolytes.
4. Completed a preliminary dendrite growth model.
5. Demonstrated that high anode film resistance leads to reduced rate capability in Li-ion batteries.
6. Measured entropy change during intercalation of Li into $\text{Li}_y\text{Mn}_2\text{O}_4$, $\text{Li}_y\text{Al}_{0.2}\text{Mn}_{1.8}\text{O}_4\text{F}_{0.2}$, $\text{Li}_y\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_2$, and graphite electrodes.

TASK STATUS REPORT

PI, INSTITUTION: A.M. Sastry, University of Michigan

TASK TITLE - PROJECT: Modeling - Failure Mechanisms in Li-ion Systems: Design of Materials for High Conductivity and Resistance to Delamination

SYSTEMS: Low-Cost Li-Ion

BARRIER: Short lithium battery lifetimes

OBJECTIVES: The primary objective of these studies is to explain and predict the role of conductive and mechanical failures on reduced performance in the baseline systems, by tightly coupled experimental and simulation studies of microscale transport and mechanics phenomena.

APPROACH: Correlation of delamination, high impedance and temperature/structure/function phenomena with specific materials composition and morphology will be developed, making use of the extensive software developed for tracking mechanical and conductive losses in heterogeneous materials at UM. Specific comparisons will be undertaken, using cells provided by the ATD and BATT programs.

STATUS OCT. 1, 2000: We developed finite element representations of model carbon materials, and developed a means for measuring conductivity of thin electrodes.

EXPECTED STATUS SEPT. 30, 2001: We expect to confirm structure/function relationships in ATD Gen 1 and Gen 2 cells, through image analysis and testing, with verification from finite element simulations.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONE: We expect to test DOE ATD Program Gen 1 and 2 cells, provided by Argonne National Laboratories, by May 31, 2001 (start date: 2/01).

ACCOMPLISHMENTS TOWARD MILESTONE OVER LAST QUARTER:

1. Initiated modeling of mechanical stresses in BATT and ATD Program electrodes.
2. Developed numerical codes to analyze multiphase carbon-binder arrays.

TASK STATUS REPORT

PI, INSTITUTION: J. Evans, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Modeling - Thermal Modeling of Li Batteries

SYSTEMS: Li-polymer (Li-ion)

BARRIER: Thermal management and safety issues, battery efficiency

OBJECTIVES: The objective is the ability to predict the thermal behavior (including stability) and efficiency of Li batteries for use in electric or hybrid vehicles.

APPROACH: The approach is a combination of mathematical modeling and experimental measurement. The modeling couples the numerical solution of the equations for heat generation and transport within a battery to the equations describing battery electrochemistry. The experiments are to measure fundamental properties for input into the model or for comparison with model predictions. Thermal conductivities of cell components are measured, as are heat generation rates, in laboratory and commercial cells.

STATUS OCT. 1, 2000: A coupled mathematical model had been developed and found to show a reasonable fit to limited experimental data on heat generation during discharge of laboratory Li-polymer cells.

EXPECTED STATUS SEPT. 30, 2001: Refinements of the mathematical model will be completed. The electrochemical calorimeter will be used to measure the heat generation rate of a limited number of commercial Li-ion batteries.

RELEVANT USABC GOALS: 75-80% discharge efficiency, thermal loss 15% of capacity in 48hrs, safety.

RELEVANT USABC GOALS: Tolerance to abusive operating conditions.

MILESTONE: Completion of measurements on Li-polymer cells available under the BATT program - September 2001

ACCOMPLISHMENTS TOWARD MILESTONE OVER LAST QUARTER:

1. Initiated calorimetry studies of BATT Program cells.
2. Preliminary analysis (using the well-known Biot number = hL/k) indicated that heat conduction processes will dominate over heat convection processes in BATT Program batteries.